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Deterioration rates of metal and concrete structures in coastal environment of the South and Northeast Brazil: case studies in the Pontal do Sul, PR, and Costa do Saupe, Bahia

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Abstract

This research presents a comparative study between two Brazilian regions with different characteristics that is the case of the South coastal area Pontal do Sul (ACS PS), located on the Paraná State and Costa do Saupe (ACS CS), located in the Bahia, Brazil. For this, were installed 2 atmospheric corrosion stations (ACS) and exposed 4 specimens of metals (aluminum, carbon steel, galvanized steel and copper) used in distribution networks, and reinforced concrete structures like utility crosshead to test the performance of additives such as silica fume, metakaolin, tire rubber and polymeric fibers, and assess both quantitative and qualitative means of aggression against corrosion from the atmosphere in function of time exposition. During this, there was the monthly monitoring of the levels of chloride and sulfate, as well as meteorological data, in order to obtain subsidies for classification of atmospheric corrosivity. The ACS PS was classified as rural atmosphere, the lowest category of aggressiveness (C_1), based on the time of wetness and the concentration of pollutants while ACS CS was described as marine (C_4). The most suitable material for this region was the aluminum, followed by galvanized steel. Already, on ACS PS, copper degraded less than the other, on average.

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1. Introduction

Like most areas of colonial America, the first population centers in Brazil were established in coastal areas, since the colonization of new lands took place by sea. The European mercantilist expansion port centers relied heavily on the pioneers, who were the links between the flows of raw material land and sea. At the end of the colonial period, was observed in the coastal port cities of Brazil are relatively isolated, consisting of local production centers or endpoints of specific production systems of the interior. Far from large centers formed with these intentions, which is the case of Rio de Janeiro, Salvador, Recife and São Luís, for example, vast stretches of coastline still remain isolated and not very busy. The construction of railway lines in the early twentieth century had them minimized the locational advantages of the coastal zone for the site, which went on to assess other factors, especially the proximity of energy sources and/or raw materials, starting a step of urbanization facing the interior, whose best example is the urban growth observed in São Paulo. In the first half of this century, there was a large number of "dead cities" being on the edge of the Brazilian coast, which will be on the areas of harassment of the outbreak of the occupation of the coastal zone, which will occur in the second half. Several processes will act in the urbanization of the coastal region from the 50s, driven by different social conditions. Analyzing the current profile, it could be seen an appeal of the coastal population located in Brazil, since, except for the border states, in every other occupation of the coast is well above the state average. Today, the coastal area hosts five of the nine largest metropolitan regions of Brazil (Fortaleza, Rio de Janeiro, Salvador, Recife and Belém) [1].

The seaside atmosphere is extremely aggressive for engineering materials. Due to the high cost of atmospheric corrosion losses, equivalent to about half of the total cost was developed the project "Ibero-American Map of Atmospheric Corrosivity", aiming to characterize and classify the atmospheric corrosivity of various test stations distributed in the countries of Ibero-American community [2].

Studies have shown that the global total spending on problems related to the degradation of materials reaches 5% of Gross National Product, and that these, about 20-25% of the costs could be avoided if they used appropriate control technologies [3]. In Brazil, it is estimated to be around U.S. $ 15 billion a year the expenses for the corrosive processes, and about $ 5 billion could be saved through the use of methods of prevention and control [4].

The atmospheric corrosion can cause severe damage to metal structures and equipment. The effects are so significant that the cost of atmospheric corrosion in China were approximately half the total annual costs to all types of corrosion of materials [5]. In recent decades, research on atmospheric corrosion were dominated mainly by field tests, which compare the resistance of different materials, the rate of corrosion in different environments, and their empirical correlations with meteorological parameters. It is not recommended to study the atmospheric corrosion without preliminary study of the meteorological and environmental aspects that affect thereon, since the contaminants have varying proportions, which will depend on the proximity of the sources and the local conditions and a high-content particulate matter, the action of the wind can act as an agent disseminator of degradation by erosion [6]. As the metallic materials, reinforced concrete structures are also degraded in harsh environments. The metal contained inside is usually achieved by salts from the external area in times longer than those considered for the unprotected metal surface, but degrade or oxidize and cause losses of major consequence to society. The deterioration process in this structure mainly depends on the inputs, the type and quantity of cement in strength, water/cement ratio being higher at higher concentrations of water, the likelihood of increased porosity of the resulting concrete, the thickness concrete covering the armature, the manufacturing process, the time of the wet surface and the external pollutants [7].

In this research different specimens of four metals used in power distribution networks (copper, carbon steel, galvanized steel and aluminum) and also of concrete, were analyzed in two coastal environments in

Brazil. One located in Northeastern Brazil, Salvador, in the region of Costa do Sauípe (ACS CS), Bahia state, and the other in the Southern region, in Pontal do Sul (ACS PS), belonging to the coast of Paraná state. For carbon steel, a large number of studies were performed by connecting the corrosion rate with sulfate concentrations, but few have linked these rates to the concentration of chloride ions and the wet and dry periods which are the main references investigated in the project, by characteristics of the studied sites [8, 9]. Being a copper material most commonly used by human society in electrical distribution networks in the electronics industry, communication networks, among others, the studies on compounds in relation to atmospheric corrosion have been very common in the last century [10]. Already, galvanized steel, has its use in the protection of large steel structures in the electricity sector, among others, such as transmission line towers, light poles and fixtures such networks. Aluminum, in turn, has been used to replace the copper metal, high-power commercial by reason of theft, vandalism, risk of death and high demand for maintenance. The concrete at its cost and lifetime high came to light during the century much of the industry, being used on poles. The two regions have different climatic characteristics considered. Pontal do Paraná is classified as a subtropical humid, with a predominance of Atlantic polar mass, mass being affected by tropical sea. The climate is controlled by air masses from tropical and polar. The average annual temperature in the region is (21 ± 1) º C and annual rainfall between 1,500 to 2,000 mm, with no dry season. The rainy season is summer [11]. For the study, was set up a station atmospheric corrosion (ACS) to approximately 300 m from the sea, near the Southern of Paranaguá Estuarine Complex in Marine Studies Center, Federal University of Paraná. The other ACS was in the metropolitan region of Salvador (MRS), in Sauípe, about 250 m from the sea. The coastal climate is humid, with about 2,466 hours of sunshine a year, ventilated (annual winds with average speed of 2.2 m/s), controlled by air masses from equatorial and tropical, but influenced by the mass maritime tropical. The average annual temperature is 25 º C and with an annual average humidity of around 81%. The time of the wet surface is very high (>> 4,000 h/year), classified as recommended by the NBR 14643/01 [12] as high corrosive environment (C_4) [4]. Winter is the rainy season [11].

2. Experimental

2.1. ACSs

The introduction of natural weathering stations aimed at evaluating the aggressiveness of atmospheric contaminants, allied to local climatic conditions on the performance of test metal and concrete, for two different regions of Brazil. In the Northeast, the ACS CS was located in Costa do Sauípe, SMR, with the coordinates 12°26.615 S and 37°55.5045 W. Already, in the South, the station was at the CEM, in the resort of Pontal do Sul in the city of Paraná, Brazil. Both are on the coast at a distance less than 500 m from the sea, to investigate the action of marine aerosols over the exposed materials. The project began in August 2009, when metal plates were exposed to a panel of natural weathering on the ACS PS. These samples were of standard metals: carbon steel, copper, aluminum and galvanized steel. The panels were installed according to ABNT NBR 6209 [13]. The samples had an average area, approximately, 31,000 mm^2. Before being exposed, were cleaned with acetone, weighed and measures of length, width and height, according to ABNT NBR 6210 [14], and a chemical cleaning. A plate of each material was removed every three months, in order to quantitatively assess the corrosion process. The samples were made of galvanized steel, carbon steel (substrate) and coated with hot dip zinc with the layer thickness of 80 μm. After the exposure period, the samples were passed by previous visual inspection, photographic documentation and proper cleaning of the corrosion products according to each type of material. The cleaning methods were performed according to the ABNT NBR 6210 [14] and ASTM G1-90 [15]. The corrosion rate (Eq. 6) was obtained by a calculation which relates to final weight and the initial.

$$\textit{Corrosion rate} = (KM/St\rho) \qquad (6)$$

Where (K) is a constant which determines the drive of the corrosion rate; (M) is the weight loss in g to the nearest mg, (S) is the area in cm^2 of the sample to the nearest 0.01 cm^2, (t) is the exposure time in h (ρ) is the specific mass in g/cm^3.

2.2. Atmospheric contaminants

The determination of the airborne salinity represented by chloride deposition rate in the atmosphere (soluble chlorides as those from the industrial or marine atmosphere aerosols) was carried out in accordance with NBR 6211 [16] which prescribe the moist candle method. The results were expressed in mg of Cl^-/m^2 a day.

A change in the design proposed method is included where the chloride ion was quantitatively determined by ion chromatography method instead of the volumetric titration aliquots of a solution of mercuric nitrate in the presence of mixed indicator difenylcarbazone-bromophenol blue, to the stop turning, blue-violet, by the formation of the complex-difenylcarbazone mercury. The advantage is to exploit other anions, also soluble in the adsorption system [6].

The determination of the sulfate deposition rate was carried out in accordance with NBR 6921 [17], which prescribes the gravimetric determination of sulfate deposition rate in the atmosphere obtained by the oxidation or fixation of sulfur-containing substances (SO_2, SO_3, H_2S and SO_4^{2-}) on a reactive surface. The results were expressed in mg of SO_2/m^2 per day.

As indicated in the previous section, their quantitative determination was also obtained by the technique of ion chromatography, rather than that indicated in the standard itself.

2.3. Meteorological data collection

The meteorological parameters used were: temperature, wind speed and direction, precipitation, radiation and relative humidity. Meteorological data were provided by the Physical Group of Paraná (CEM) at the Universidade Federal do Paraná, while in Bahia these data were obtained from meteorological station installed in ACS. The degree of corrosive atmosphere followed patterns NBR 14643 [12], compared to metallic materials analyzed and characterized the atmosphere into 5 categories corrosive substance, ranging from C_1 (very low) and C_5 (very high).

2.4. Reinforced concrete structures

The study aimed to evaluate the relationship between the durability of pre-cast concrete structures (concrete crossheads for electrical distribution networks) with concrete mixtures produced with different additions, with reference values of electric potential between parts when exposed for long periods in extremely aggressive environments. For this 20 units were made of reinforced concrete in dimensions (11x11x190) cm (NBR 8451/98) [18]. The artifacts were made of concrete produced with cement CP V-ARI , consumption of 398 kg/m³, dosage (1: 1.53: 2.1: 0.5:x), as shown below and shown in Fig. 1.

- x= 0; reference concrete, without addition;
- x= 8% silica fume aided to concrete (relation to cement);
- x= 8% metakaolin aided to concrete (relation to cement);
- x= 4.75% ground tire rubber, aided to concrete (relation to cement); and
- x= 1% polyester fiber aided to concrete (relation to cement).

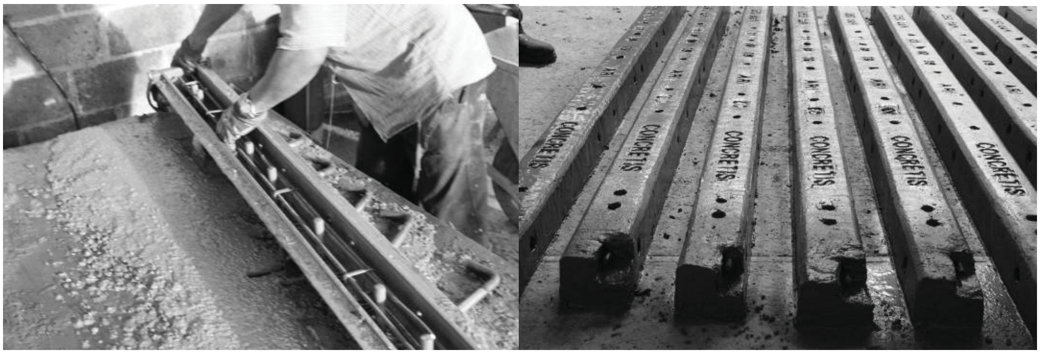

Fig. 1. Molding of concrete crossheads for electrical distribution networks

To define the dosage used in the production of concrete was chosen an industrial product of the company as a reference. To evaluate the durability of concrete studied was chose an electrochemical technique, a corrosion potential measurements, that were made periodically during the aging period.

The equipment to measure the electrochemical potentials consisted basically of: a voltmeter of high input impedance (greater than 10 MΩ) with resolution of millivolts; and a reference electrode of copper/copper sulfate.

3. Results and discussion

3.1. Rating climate and weather data

The climate of the ACS PS, according to Köeppen classification, is Cfa, subtropical humid mesothermal with hot summer. According to data from the meteorological station, the average temperature was 22.1 ° C, with maximum of 36.1 º C and minimum of 8.7 ºC. During the summer, the average reached 26.5 ° C, while in the winter was 17.4 ° C. The annual average precipitation was 0.26 mm/h, and a sum of 2,780 mm between August 2009 and August 2010. The coast of Paraná presented no dry period during the year, rainfall was well distributed, but with higher concentrations observed during the summer, with an average of 0.36 mm/h between early December and mid-February. The RH% during the period was approximately 84%, no significant differences between the different seasons. From this classification we could infer a local moderate corrosivity, which includes the region of ACS CS and ACS PS, however, one must take into account which are pollutants that print increase in corrosion rate, and are not addressed in this index. The ACS CS, according to Köppen, is a city of hot and humid climate is typically tropical. The annual average temperature was 25.2 °C. Already, the relative humidity was pretty high, ranging from 77 to 96%, with an annual average of around 81%. The capital of Bahia is a Brazilian city with the highest annual rainfall around 2,000 mm. In the climatic classification proposed by A. Strahler, Sauípe is in an area controlled by air masses equatorial and tropical. It is classified as coastal humid tropical sea exposed to the masses. You can see that in both classifications, the studied regions are divergent.

During this period, solar radiation at the site was about 2 MJ/m^2, and in the ACS PS was approximately 1.56 MJ/m^2. These values are significant in the analysis of time of wetness. The wind patterns were also observed. In both regions, the prevailing winds were from the ocean, favoring the concentration of aerosols in the coastal zone [4, 19]. The average speed observed in the ACS PS was 3.33 m/s and in the ACS CS, was 2.2 m/s. Since the direction of influence in the analysis, we calculated the mean direction from the components "u" and "v" of the winds, and the first 4 months in ACS PS, was SE-E. According to the literature (Muehe, 2006, Oliveira *et al.*, 2011), the prevailing winds were from the East, Southeast and South. According to the author, the wind speeds above 6 m/s, were mostly from South-Southeast. The predominant direction in the region of ACS CS was the Northeast, the average speeds of 7 m/s.

With respect to the values of Id, the ACS of PS showed a moderate aggressiveness with a tendency to a high of 4.21. Already, the region of Salvador (ACS CS) was very aggressive, with a value of 5.1.

3.2. Monitoring of Atmospheric Contaminants

Chloride contents

In both ACSs the chloride contents were more significant than the sulfate, due to the proximity of the ACS to the seashore. The annual average chloride concentration, in ACS PS, expressed in mg/m^2.day, was 22.8. The highest values were observed in January and February, reaching 48.3 mg/m^2.day. The minimum value was 1.4 mg/m^2.day, in June and July 2010. According to the Liesegang classification's [20], this ACS was classified as rural. Some conditions may have influenced this result. This ACS was installed in a region with low influence of breaking waves, for its proximity to the Paranaguá Estuarine Complex (CEP). The vast sandbank located in the region between the ACS and the seashore line, may have acted as a natural barrier to chloride ions. In the ACS CS the average results allowed to classified as marine environment [20], being 184 mg/m^2.day. The maximum value was equal to 514 mg/m^2.day in the months of June and July 2010, while the minimum was 29 mg/m^2.day between February, March and April of that year.

Sulfate content

In ACS Sauípe, the average annual concentration of SO_2 in the atmosphere was 18 mg/m^2.day. The maximum value was obtained during June and July 2010, equivalent to 31 mg/m^2.day, and the minimum value was 8 mg/m^2.day. Along with the concentrations of chloride in the classification of Liesegang [20], the marine environment was considered, as already mentioned. In ACS PS, the value of the rate of sulfation based on concentrations of sulfur dioxide was similar to the Northeast. The average annual SO_2 was approximately 25 mg/cm^2.dia. During the months of June and July 2010, was observed maximum value of 41 mg/m^2.day, and in January and February of that year, was recorded 8 mg/m^2.day, the lowest. In the classification of Liesegang [20], the ACS PS was considered a corrosive environment of the rural type.

3.3. Natural Weathering Tests

Aluminum

Aluminum had the tendency to have localized pits, but in most of samples analyzed from the first year the general corrosion was verified. This fact was attributed to the cleaning process of the samples before exposure, where the oxides of aluminum plates that protect it from the atmospheric ions may have been removed. Then until the passivation layer to return to form there was a large mass loss associated with general corrosion.

The maximum average value observed in ACS PS was 9.6 μm/year. This value was considered so high, relation to the other ACS analyzed in North of Brazil, in São Luiz of Maranhão, which presented average values of 4.7 μm/year [21].

In the ACS CS the values of aluminum corrosion rates decreased as the increased time of exposure of the metal in the atmosphere, even with the increased concentration of chloride ions. In Fig. 2, is presented the graph of the corrosion rate of aluminum obtained in the two ACS's as function of exposition time.

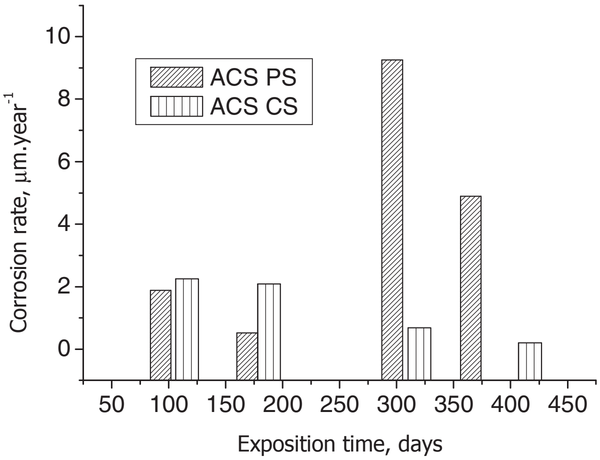

Fig. 2. The corrosion rates of aluminum metal in the ACSs CS and PS as a function of time exposition

Copper

Copper was the only analyzed material that degraded more, on average, in the ACS CS to the ACS PS. It was observed that even with increasing concentrations of chloride, a reduction of weight loss of copper in the coast of Bahia, from the time of the exposition. The aggressiveness of the environment was very high for this metal, being on average higher than the degradation observed for aluminum, C_{5+}. The same consideration of the cleaning process of the samples of aluminum were used in this case, with the removal of the oxide layer adhered on the surface thereof. After the passivation layer formed on the surface of the material, even with the increase of air pollutants, which occurred in ACS CS, degradation of the metal was lower.

In ACS PS, the degradation of copper was lower in the summer months, perhaps the greatest concentration of rain, acting washing the ions from the metal surface. The material was on average less degraded of the four metals studied, which was the most appropriate after one year of exposure. The classification of aggression resulting C_4 was classified as high. In Fig. 3 presents the corrosion rates in the two ACS's, which can be analyzed the effect of passivation, especially in ACS CS, by decreasing the corrosion rate itself over the period of exposure of metal to the environment.

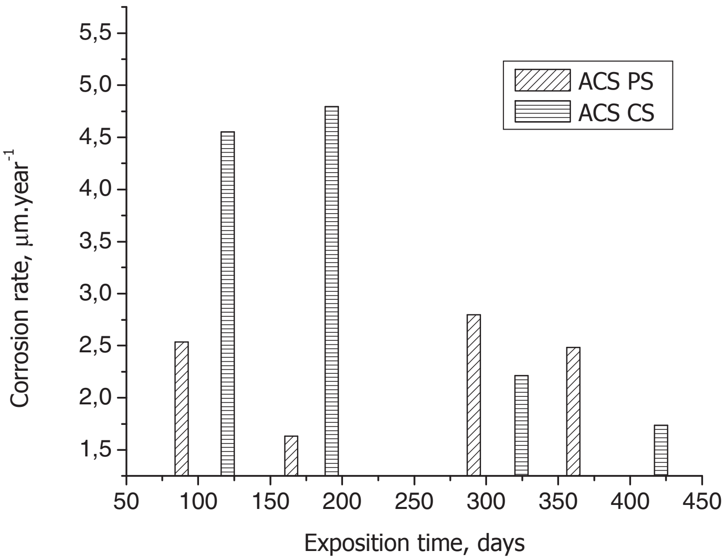

Fig. 3. Comparison of the corrosion rates of copper, in function of time exposition

Carbon steel

The atmospheric degradation of carbon steel depends mainly on the time of wetness, or the temperature and RH%, beyond on polluting the atmosphere, which accelerates the process. In more aggressive environments, there is a great tendency to formation of corrosion products that passive material after 14 months of exposure, as observed in Colombia, a tropical country in Latin America [22].

In the ACS CS, it was observed a reduction in corrosion rate as a function of exposition time, possibly generated by the protective oxide layer adhered to the metal surface. In Fig. 4 is shown a graph resulting from the measures of rates of metal corrosion. The aggressiveness of the environment C_5 ACS PS was considered high. For example, in Spain, in the region of Jinámar, subtropical, in a marine industrial, i.e., more aggressive in terms of pollution, the degradation of carbon steel reached only C_4, with the results indicating the concentration factor as a main of chloride ions [23]. In a study of atmospheric corrosion in Vietnam, in places exposed, it was seen that the mass loss of carbon steel cannot be explained by concentrations of SO_2 and chloride, which did not show specific factor to explain the process [24].

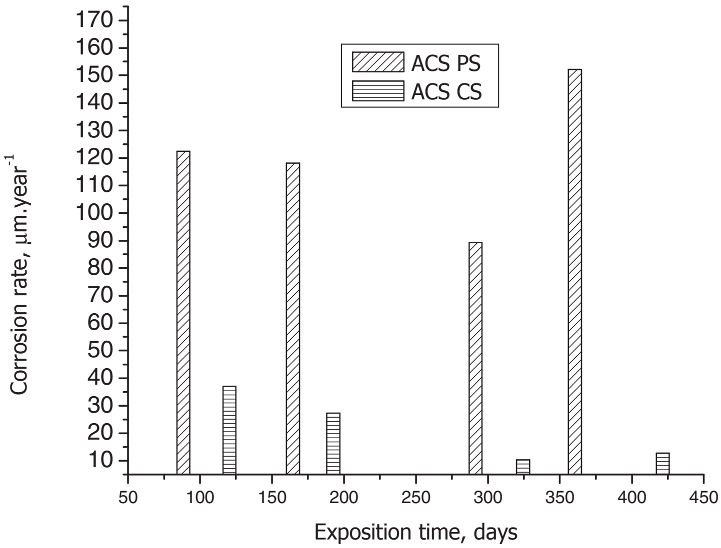

Fig. 4. Comparing the corrosion rates of carbon steel, in function of time

Galvanized steel

The zinc coating protection of the carbon steel is very effective to increase the life time of the material. In ACS CS, galvanized steel was the second material that on average more resist corrosion from the atmosphere, just behind the aluminum. In ACS PS, galvanized steel had less weight loss than aluminum.

The classification of the ACS PS was high aggressiveness (C_4) and mean (C_3) in the Northeast. In literature, there are studies that show that the degradation of zinc is strongly linked to the presence of moisture, existing rural areas that have higher rates than industrial centers, as observed in Cuba. The zinc corrosion products, mainly formed from sulfate, are soluble in water and rain water is important for action in washing the surface of the plates. The corrosion rates for galvanized steel under exposed and housed showed that the last one has caused greater weight loss [13].

A pattern can be seen in Fig. 5 that is the characteristic tendency of most test materials exposed to natural weathering, which is the decay rate of corrosion over time [25]. This does not indicate that the degradation will decrease, but it shows that there may be a decrease in its corrosion rate, but this fact does not prevent the loss of their properties, especially mechanical.

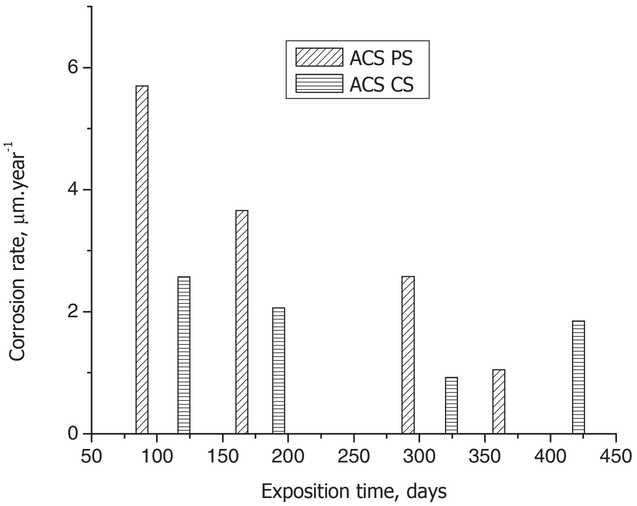

Fig. 5. Comparison of the rate of corrosion of galvanized steel, in function of time exposition at ACSs CS and PS, respectively

According to the categories estimated for the ACS PS, it was observed that the materials in the field did not behave that way. This can be explained by the cleaning of specimens before the exposure, they were removed from the corrosion products which are responsible for the passivation of some of the metal worked. The proximity of the ACS with an unpaved road may also have influenced the results, by the spraying of dust containing a mixture of silicates, silica and salts of sea water, these two last results of the road near the seafront. The comparison of corrosion rates in the two seasons of weathering can be seen in Fig. 6.

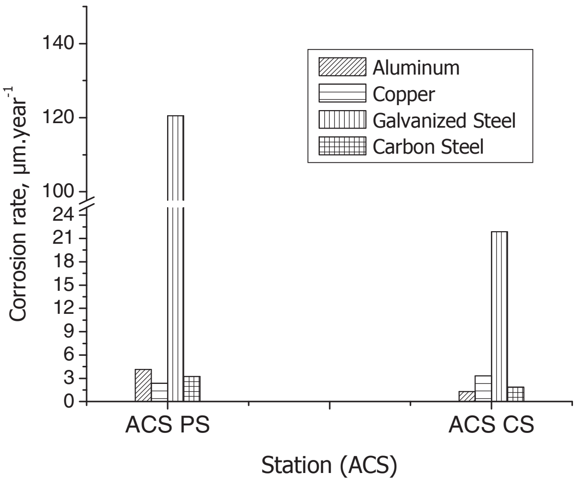

Fig. 6. Comparison of average rates of corrosion of the metal standard for the two seasons of natural weathering, after a year of exposure

Concrete structures

The corrosion potentials were followed for about a year and a half after exposure of the utility crosshead, and continue to be monitored, both in the region of ACS CS and PS, respectively. Because it is a qualitative method, this time exposition period was not sufficient to infer which specimens behave better. According to measurements taken for two ACSs, the reinforced steel samples still in a passive state of corrosion, with values ranging between 0 and -200 mV [26].

In Fig. 7, is presented by way of illustration, a curve regarding the potential for corrosion of the concrete with a utility crosshead reference (no additions), exposed in ACS PS within 1 year. There was, as mentioned, low or no one corrosion process started [26].

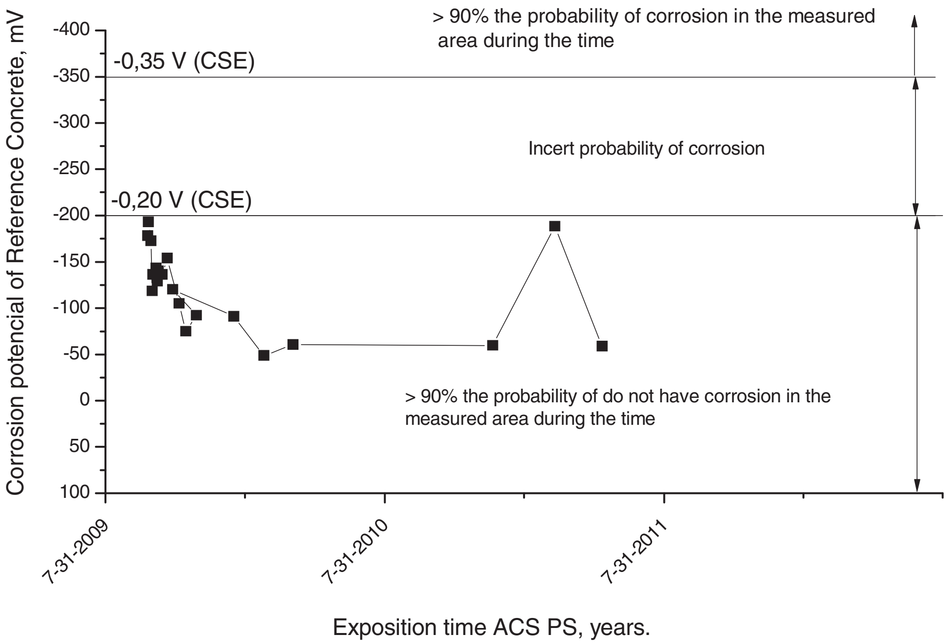

Fig. 7. Corrosion potential of a utility crosshead made as reference concrete, installed in ACS PS, during 1 year of time exposition

4. Conclusions

From the corrosion rates of standard metal - aluminum, copper, carbon steel and galvanized steel - after one year of exposure in two ACSs, specifically of ACS CS and ACS PS, in Northeast and South of Brazil, respectively, were possible to determine the corrosivity of their environments. On the ACS PS was observed aggression too high for carbon steel and aluminum (C_5) and high (C_4) for copper and galvanized steel. The estimated time-based corrosion of the wetness, chloride and sulfate indicated, in turn, moderate aggressiveness (C_3).

In the region of ACS CS, only aluminum behaved as estimated by the technical standard [12], with high corrosivity (C_4). Copper presented mass loss equivalent to aggressive environments as very high (C_5), carbon steel, as low (C_2), and galvanized steel, moderate (C_3).

The ACS PS region was more aggressive for three of the four metals exposed, given that the average corrosion rates of the four plates taken from each metal, copper only lost more weight in ACS CS than in

ACS PS. Such behavior may be a consequence of the street traffic, and unpaved which is far less than 50 m of their ACS, with a lot of dust (clay, silica, and also, chloride salts). The Id presented degradation process between moderate to high for the ACS PS region, observed in the rates of corrosion of metals, and very high for ACS CS, which was only observed in specimens of copper. The analysis of meteorological data pointed to high moisture content in both seasons, which will favor the degradation processes. The predominant wind direction was from the sea towards the coast, which has helped to increase the concentrations of chloride ions. The climate in the MRS was characterized by two well defined seasons, the dry season, from September to March, and rainfall, April to August. Already, on the coast of Paraná, at ACS PS there existed two distinct seasons, with rainfall well distributed throughout the year, with the rainy season in summer.

The material presented, on average, the lowest corrosion rates in the South was copper, followed by galvanized steel and aluminum. Already, in the Northeast, aluminum was the most resisted, on average, to air pollutants, with better performance than galvanized steel and copper, respectively. It should be noted, that was not evaluated in the Southern pitting corrosion and the coast of Bahia, at ACS CS this was significant for aluminum [4]. The carbon steel was the most had weight loss in both regions, especially at ACS PS, where corrosion was higher than that observed in marine-industrial environments subtropical regions, as in Spain, for example, the ACS of Jinámar. The contents of chloride and sulfate can be classified according to Liesegang [23], the region of the marine environment as ACS CS, aggressive C_4, and the ACS PS as rural, with aggressiveness C_1. The proximity of the coast, the chloride ions were more significant than the sulfate ions, characteristic, especially in industrial regions. With respect to the utility crosshead of reinforced concrete, and its additives, nothing could be inferred in the research, since the electrochemical method used is qualitative and not allowed to predict the service life of structures, but only if the samples have gone to the active state corrosion. After a year and a half of collections, did not alter the potential for regions of higher probability of existence of the corrosion process.

Acknowledgements

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